17

RAMAN SPECTRA OF BENZENE AND CARBON-DISULPHIDE AT —209°C

S. C. SIRKAR, D. K. MUKHERJEE and P. K. BISHUI

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
CALCUTTA-32.

(*Received, May 5, 1964*)

Plate VI

ABSTRACT. The Raman spectra of crystals of benzene and carbon-disulphide at −209°C have been investigated using liquid nitrogen boiling under reduced pressure as the refrigerant. At −209°C benzene gives five low frequency lines at 62, 82, 91, 100 and 134 cm^{-1} respectively. It has been pointed out that the heat capacities calculated for the crystal below 70°K upto 4°K, agree well with observed values by choosing three frequencies 64 cm^{-1}, 100 cm^{-1} and 134 cm^{-1} for three Einstein functions and taking into account a Debye function as pointed out earlier.

From a study of the structure of crystals of benzene at -3°C it has been concluded that due to attraction between the π -electron of any ring and the hydrogen atom of the neighbouring molecule the planes of every pair of adjacent molecules in the (010) plane are almost perpendicular to each other and they are inclined to the b-axis. The low-frequency Raman lines have been attributed to the angular oscillations of such individual molecules attached to each other through hydrogen bonding.

In the case of carbondisulphide also, the two lines at 73 cm^{-1} and 81 cm^{-1} have been assigned to angular oscillations in molecules forming polymeric chains in the crystal through S....S bonding parallel to one of the diagonals of the (001) plane of the tetragonal unit cell.

INTRODUCTION

The Raman spectrum of single crystal of benzene was first studied by Gross and Vuks (1935) and two new lines at 63 and 108 cm^{-1} were observed by them. The lines were attributed to lattice oscillations. One of the present authors (Sirkar, 1936) observed three new lines at 81, 98 and 124 cm^{-1} respectively in the Raman spectrum of frozen benzene at −180°C. He concluded that the new lines shift away from the Rayleigh line and a new line appears when the crystals at a temperature just below the freezing point are cooled to −180°C. He suggested that probably these lines were due to oscillations in groups of molecules formed by intermolecular association in the solid state. Sirkar and Gupta (1938) pointed out that the heat capacities of crystalline benzene at low temperatures observed by previous workers could be explained by assuming a Debye function with θ' equal to 121.5°K and taking into account the three Einstein functions corresponding to the three Raman shifts 81, 98 and 124 cm^{-1} respectively.

The Raman spectrum of single crystal of benzene at a temperature just below the freezing point of the liquid was next investigated by Kastler and Fruhling (1944). They observed four new lines at 35, 55, 65 and 100 cm^{-1} respectively in place of the two lines reported by Gross and Vuks (1935). Rousset (1944) calculated the heat capacities of the crystal at low temperatures assuming the line 35 cm^{-1} to be due to free rotation of the molecule about an axis perpendicular to the plane of the molecule and taking Einstein functions corresponding to the other three frequencies and also a Debye function with θ' equal to 1150°K.

The Raman spectrum of a polycrystalline mass of benzene at −180°C was re-investigated by Sirkar and Ray (1950) and they observed five new lines at 47, 53, 78, 95 and 134 cm^{-1} respectively. Assuming these lines to be due to two molecules associated to each other and the line 95 cm^{-1} to be a doublet, they calculated the heat capacities of the crystal upto 4°K taking Einstein functions corresponding to three Raman shifts 58, 90 and 135 cm^{-1} respectively and a Debye function with θ' equal to 121.5°K. They observed that although the calculated values of C_v were slightly less than the observed values of C_p reported by Ahlberg *et al.* (1937) in the ranges from 4°K upto 10°K and also above 50°K, the calculated values were larger than the observed values for temperatures from 20°K upto 40°K. They suggested that the lowest frequency corresponding to the line 53 cm^{-1} observed for the crystal at −180°C might shift to 64 cm^{-1} at temperatures below 40°K and in that case the heat capacities calculated on the above assumptions would agree satisfactorily with the observed values.

The study of the Raman spectra of many other organic compounds in the solid state at different temperatures below their freezing points has shown that the new lines in the low frequency region undergo changes in their positions and intensities with lowering of temperature of the crystals upto about −180°C.

The changes observed in the spectrum of crystals of para-dichlorobenzene by Ray (1951) with changes in temperature upto −180°C indicate that some irreversible change in the spectrum takes place with lowering of temperature of the crystals upto −180°C. It was not known, however, how the spectra would change with the lowering of temperature below −180°C. An attempt was therefore, made to make an arrangement for studying the Raman spectra of frozen organic compounds at about 64°K and the results obtained in the case of benzene and carbon disulphide are discussed in the present paper.

EXPERIMENTAL

The refrigerant used for lowering the temperature upto 64°K was liquid nitrogen boiling under reduced pressure. The liquid nitrogen was supplied by Indian Oxygen Ltd. The arrangement for photographing the Raman spectra at 64°K is shown in Fig. 1 in which the sources of light used for illuminating the subs-

tance have been omitted. The mouth of the transparent Pyrex glass Dewar

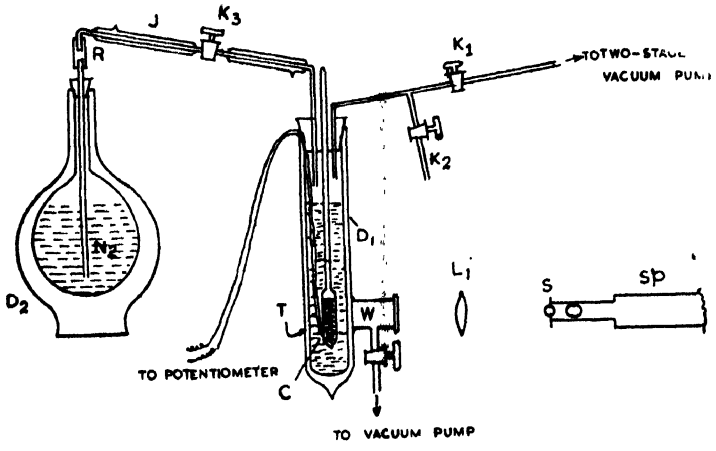


Fig. 1

vessel D_1 is closed with a cork which is sealed with soft sealing wax. The vertical limb of the bent Pyrex glass tube provided with the stop cocks K_1 and K_2 enters into the vessel D_1 through the cork upto a certain depth and the other end is connected to a high vacuum pump. The tube containing the sample is suspended inside the vessel so that its lower part rests in front of the window W. The open end of a wide and short glass tube with one of its ends closed with a glass plate is placed on the window and sealed with sealing wax. The tube thus closed at both ends is evacuated through a side tube connected to it so that no moisture can be deposited on the window when the Dewar vessel D_1 is filled with liquid nitrogen. A third tube with its two ends bent as shown in the figure connects the Pyrex glass Dewar vessel D_1 with the metallic Dewar vessel D_2. This tube is provided with a large stop cock K_3 near its middle and the portions of the tube on both sides of K_3 are double-walled, the regions between the two walls being evacuated. One of the short vertical limbs of the bent tube is connected through a rubber tube to a long narrow Pyrex tube which dips into liquid nitrogen contained in D_2. The other end enters into D_1 through the cork. At first the stop cocks K_2 and K_3 were closed and the vessel D_1 was evacuated. On opening K_3 liquid nitrogen was drawn into D_1 till the surface of the liquid rose upto a height below the lower ends of the two tubes which enter into D_1 through the cork. The stop cork K_3 was then closed and after some time the temperature measured with a copper-constantan couple was found to be almost constant. The constants of the thermocouple were determined by using the melting point of toluene, the boiling point of liquid oxygen and the boiling point of liquid nitrogen at atmospheric pressure as standard temperatures. When the crystals C formed inside the container attained this steady temperature the container was illuminated by light from two vertical mercury arcs which were focussed on the container

with the help of two wide glass tubes filled with distilled water. A fuess glass spectrograph giving a dispersion of about 12A/mm in the 4047A region was used to photograph the spectra. The exposure required varied from two to two and a half hours. When liquid nitrogen in D_1 was replenished the slit of the spectrograph was kept closed and it was opened again when the pressure in D_1 was sufficiently reduced by the pump. The lowest temperature attained was found to be $-209°C$. The Raman spectra of benzene and carbon disulphide at this temperature were photographed using the arrangement mentioned above. The spectra of the compounds at $-180°C$ were also photographed using the same spectrograph in order to compare the results with those for the substances at $-209°C$.

TABLE I

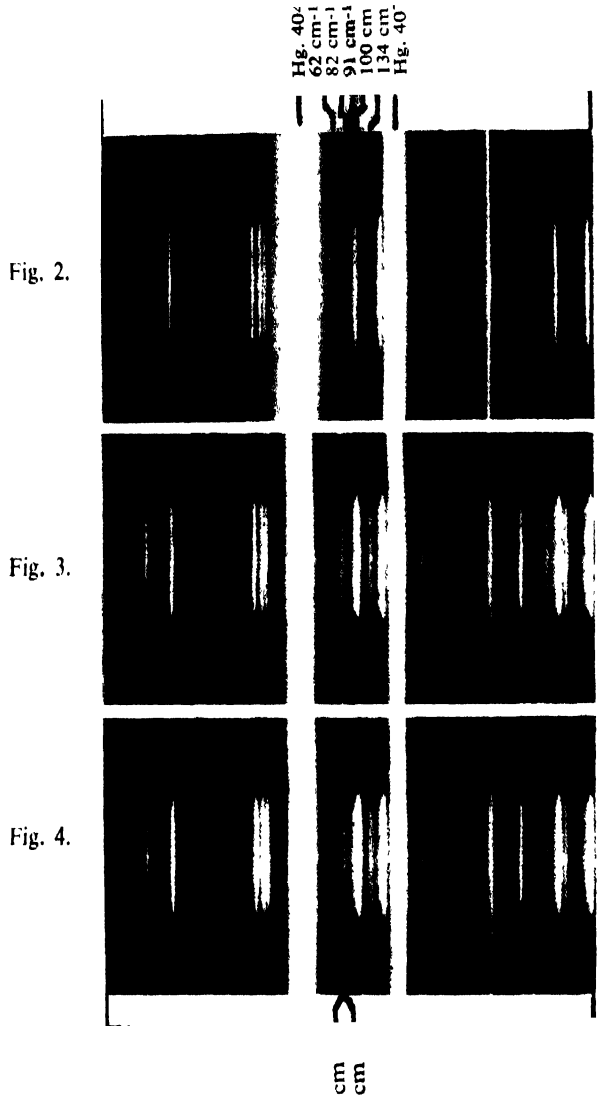
Raman spectra of C_6H_6 and CS_2; $\Delta\nu$ in cm^{-1}

C_6H_6 at -180°C Sirkar and Roy (1950)	C_6H_6 at -209°C Present authors	CS_2 at -183°C Present authors	CS_2 at -209°C Present authors
47 (1)			
53 (2)			
	62 (3)		
		70 (15)	73 (10)
78 (5)	82 (5)	81 (3)	81 (2)
95 (1b)	91 (1)		
	100 (1)		
134 (3)	134 (3)		
603 (1)	605 (1)		
		656 (6)	658 (4)
		804 (2)	805 (1)
855 (2)	858 (2)		
989 (10)	992 (10)		
1174 (4)	1176 (4)		
1581 (3)	1584 (2)		
1602 (2)	1605 (2)		
3042 (2)	3046 (4)		
3046 (2)			
3063 (5)	3063 (4)		

RESULTS AND DISCUSSION

The spectrograms for benzene and carbon disulphide are reproduced in Figs. 2, 3 and 4, Plate VI. The Raman shifts are given in Table I.

A comparison of the frequency shifts of benzene observed for the crystal at $-180°C$ and $-209°C$ shows that a significant change takes place in the positions of the lines in the low frequency region with the lowering of temperature from $-180°C$ to $-209°C$. The lines 47 and 53 cm^{-1} are replaced by a single line



Raman Spectra

Fig. 2. Benzene at −209°C.
Fig. 3. Carbondisulphide at −180°C.
Fig. 4. ,, at −209°C.

62 cm^{-1} and also the line 95 cm^{-1} splits up into two lines at 91 cm^{-1} and 100 cm^{-1} respectively with the lowering of temperature. Thus the predictions made by Sirkar and Ray (1950) that at temperatures below 40°K the lowest frequency of vibration might increase to 64 cm^{-1} and the line 95 cm^{-1} might split up into two lines are proved to be correct by the results. The results also support the conclusion that Einstein functions corresponding to three of the low frequency lines together with a suitable Debye function explain the heat capacities of the crystals of benzene from 70°K upto about 4°K quite satisfactorily.

In order to understand how three new modes of vibration of the molecule with such low frequencies arise in the crystal it is necessary to take into consideration the orientation of the molecules in the lattice given by Cox and Smith (1954) in the case of the crystal at −3°C. The photograph of a model of the upper half of the unit cell made in accordance with the structure reported by them is shown in Fig. 5. The normal to the molecule at each corner of the ortho-

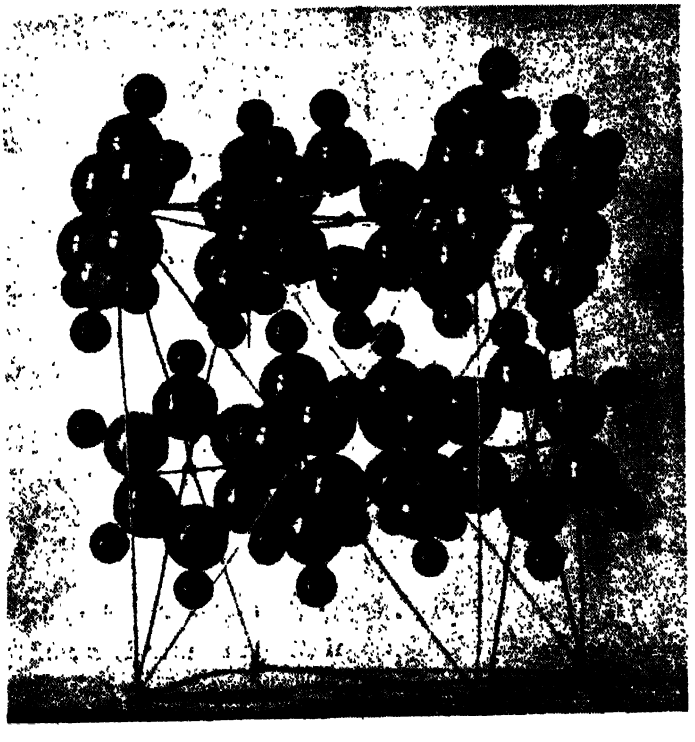


Fig. 5

rhombic unit cell is inclined at 48° to *c*-axis and at 77° to *b*-axis. The latter axis is vertical in Fig. 5. The other three molecules in the unit cell are derived by the two-fold screw axes parallel to *b*-axis at distance *a*/4 in the (001) plane and also similar axes in the (010) and (100) faces parallel to *a*-axis at a distance c/4

and to *b*-axis at a distance c/4 respectively. The cell is a pseudo-face-centred one, the molecules at the centre of faces being turned with respect to those at the corners of the unit cell. It can be seen from the model that the planes of all the molecules are only slightly inclined to the *b*-axis, the angle of inclination being 13°, but no two adjacent molecules in the (010) plane are parallel to each other. In fact, every molecule in this plane is surrounded by its four nearest neighbours oriented in such a way that the angle between the normal to the plane of the molecule and that to any of its four neighbours is either about 82° or about 92°. The density of the crystal at −3°C is about 1.08 g/cc.

It is a significant fact that the adjacent molecules in the (010) plane are not parallel to each other and also they are not parallel to *b*-axis so as to form a tetragonal lattice. The orientation shown in Fig. 5 indicates an attraction between the hydrogen atom of a molecule at the corner of the unit cell and the nearest carbon atom of the molecule at the centre of the (010) face. Probably the π-electrons of the carbon atoms are responsible for such an attraction. The small tilt about a diagonal of the (010) face diminishes the distance between the two such atoms lying below the (010) face on one side of the centre of the face and that between two such atoms lying above the (010) plane on the other side. The shortest distance between the centres of the hydrogen atom and the carbon atom mentioned above is about 2.72A. It appears that whenever two benzene molecules try to approach each other their planes become almost mutually perpendicular to each other due to the attraction between the hydrogen atom of one of the molecules and a carbon atom of the other molecule. If this process is repeated in two almost mutually perpendicular directions a sheet of molecules form the (010) plane. It is evident from the structure that when the other such sheets parallel to (010) plane are arranged one above the other the shortest distances between the carbon atoms in the upper half of the molecule at the centre of the (010) face and the hydrogen atoms of the neighbouring molecules at the centres of the other two faces and at the corner of the unit cell are the same and have a value about 2.72A. Similar distances occur also in the case of the lower half of the molecule at the centre of the (010) face.

Since there is a centre of symmetry at the centre of each molecule any translational oscillation of the molecules against each other is forbidden in Raman effect. The four lines at 35, 55, 65 and 100 cm^{-1} observed by Kastler and Fruhling (1944) are therefore due to angular oscillations of the molecule. The first line may be due to such an oscillation about an axis perpendicular to the plane of the molecule. This axis almost coincides with a diagonal of the (010) face of the unit cell. The lines 55 and 65 cm^{-1} are probably due to angular oscillation of the molecule about the other diagonal of the (010) face, the splitting arising from the slight difference between the molecule at the corner of the unit cell and that at the centre of the (010) face introduced by the deviation of the unit cell from the

tetragonal form and by the inclinations of the molecule to the *b*-axis. The line 100 cm^{-1} may be due to an oscillation about the *b*-axis of the crystal.

The crystal structure of benzene at −180°C or at still lower temperatures is not known. The lines 62, 82, 91, 100 and 134 cm^{-1} given by the crystal at −209°C are also due to such oscillations. It appears that frequencies of these oscillations increase and some of them are split up into two frequencies at the lower temperature. The angles between the normal to the molecule and the *c*-axis and *b*-axis may be greater than 48° and less than 77° respectively at −209°C. In that case the primitive translation along *c*-axis may be much less than 7.05A found for the crystal at −3°C. The contraction of the lattice at the low temperature is expected to make the shortest C...H distance less than 2.72A, and therefore, the strength of the C...H bond is expected to increase at the lower temperature. The increase in the tilt of the molecule about the horizontal axis may increase the difference in the environment of the molecule at the corner of the unit cell and that of the molecule at the centre of the (010) face and thus there may be at most six frequencies of angular oscillation. If two of them be very near to each other only five frequencies can be observed and the five Raman lines given in Table I for the crystal at −180°C or −209°C can be accounted for on these assumptions.

It may be pointed out here that Bhagavantam (1941) and independently Kastler and Rousset (1941) proposed that the low frequency lines in the Raman spectra of naphthalene and benzene might be due to angular oscillations of the molecules, pivoted in the lattice, about their three axes. The above discussions show that formation of weak intermolecular linkage is responsible for the restoring forces required for such oscillations in the crystals of benzene, as pointed out by Sirkar (1951). Table I shows that the frequencies of some of the other modes of oscillation of the benzene molecule also tend to increase at lower temperatures. The frequency shift 858 cm^{-1} diminishes to 849 cm^{-1} when the crystals are melted. As this line is due to a mode involving bending of the C-H bond in a plane perpendicular to the plane of the ring the increase in the frequency at low temperatures indicates formation of hydrogen bond. The slight increase in the frequencies of some of the modes of vibration of the ring may be due to slight increase in the strength of the C-C bond at lower temperatures.

The density of benzene at 20°C is about 0.879 g/cc and that of the crystal at −3°C is 1.08 g/cc. So, the volume increases by about 22% when the crystals are melted and brought to a temperature of 20°C, and therefore, each of the diagonals of the (010) plane of length 10.25A is represented by a distance 10.97A in the liquid. If the arrangement of the molecules in the crystal is assumed to persist to some extent in the liquid the molecules will generally be free to rotate about an axis perpendicular to the plane of the ring, but it may be possible for some adjacent molecules to be still linked to each other through C...H bonding